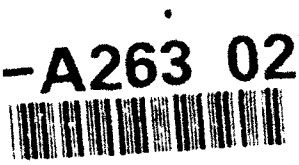

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Progress Report

June 1, 1992 to January 1, 1993

Visible Light Emitting Materials and Injection Devices

ONR/DARPA URI

Grant Number N00014-92-J-1895

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(I) Molecular Beam Epitaxial Growth (Robert Park)

(I.1) New Equipment Installations:

II-VI MBE system: An elemental sulphur and magnesium effusion sources were installed and calibrated. A second gas line and high-precision leak valve were installed on the RF plasma discharge source for generation of an atomic hydrogen beam and the hydrogen plasma was characterized using an optical emission spectroscopy apparatus.

III-V MBE system: An RF plasma discharge, free-radical source was installed on the Varian Gen II MBE system. Gas lines were installed for both hydrogen and nitrogen free-radical production. Nitrogen and hydrogen plasmas were characterized using an optical emission spectroscopy apparatus.

(I.2) Growth Related Studies:

II-VI work: In-situ GaAs surface cleaning studies were performed employing an atomic hydrogen beam generated in our RF plasma discharge source. It was found that GaAs surfaces can be cleaned readily at wafer temperatures below 400°C in contrast to conventional thermal treatment which requires processing temperatures in the vicinity of 600" C. In addition, GaAs surfaces cleaned via an atomic hydrogen beam were found to the specular, contrary to conventionally cleaned surfaces which are considerably rough on the atomic scale following oxide desorption. This work is reported in detail in a paper which has been accepted for publication in the Journal of Applied Physics.

Progress was made in our efforts to grow lattice-matched ZnSSe/GaAs epilayers as a first step towards growing lattice-matched MgZnSSe/GaAs epilayers. Difficulties have been experienced in terms of controlling the S flux from our elemental source, however close lattice-matching has been achieved under particular conditions, although defects are still visible by cross-sectional TEM implying that defect concentrations are still quite high ($\approx 10^6$ cm^{-2}). Work is in progress to improve on our control over the S content in the ZnSSe films.

III-V work: Initial efforts have focused on GaN growth on both Si and SiC-coated Si substrates using our new RF plasma discharge nitrogen free-radical source. Ex-situ wet chemical cleaning techniques were developed for both Si and SiC-coated Si wafers (SiC/Si epilayers obtained from Cree Research, Inc.). In terms of in-situ processing, our best techniques developed to date are as follows.

Si wafers - Excellent (2 x 2) reconstructed Si surfaces are obtained following heating to ≈ 700°C (between 400 and 700°C, the surface exhibits a (1 x 1) pattern). All GaN films have been grown on (2 x 2) reconstructed Si surfaces.

SiC/Si wafers - (1 x 1) SiC surfaces with well defined Kikuchi bands are obtained following heating to ≈ 820°C (our highest

substrate temperature). However, reconstruction has not been observed to date. The absence of reconstruction would imply that the SiC surfaces are not atomically clean. All GaN films have been grown on (1 x 1) SiC surfaces.

GaN growth - GaN films grown on Si over the substrate temperature range 400 to 700°C were found to be polycrystalline under regular growth conditions. However, GaN films were found to be epitaxial (zincblende) when grown on SiC-coated Si substrates at temperatures >=600°C. Faceting, however, was observed to take place in one azimuth following the deposition of ≈ 200Å of GaN on SiC/Si, although the films remained crystalline. Work is in progress with a view to preventing the occurrence of faceting in these films.

(II) MOCVD growth of II-VI materials (Tim Anderson)

(II.1) Growth of novel $Zn_{1-x}Cd_xS_{1-y}Se_y$ confinement structures: No reports of previous work could be located for the growth of Zn-Cd-S-Se films. It was thus decided to first approach the growth of the Zn-Cd-S pseudobinary material, focusing on the composition lattice matched to GaAs. A study was performed to establish the influence of growth conditions on the composition and growth rate of ZnCdS and the crystal structure.

The substrates used in the growth of ZnCdS were semi-insulating (100) +/- 0.5° and (100) 2° GaAs. GaAs was chosen as the substrate due to its wide availability and high quality. With a lattice constant of 5.654Å, GaAs makes a suitable substrate to which ZnCdS can be lattice matched. The reactants were diethylzinc (DEZn), dimethylcadmium (DMCd), and hydrogen sulfide (H_2S). Both DEZn and dimethylzinc (DMZn) are commonly used for Zn precursors, but DEZn was selected for the Zn source because the ethyl ligand is reported to minimize carbon contamination compared to the methyl ligand. The metalorganics are highly reactive with the hydride gas even at room temperature. To prevent parasitic gas-phase reactions, the group II metalorganics and H_2S were introduced into the reactor through two separate ports.

Five growth parameters were investigated: (1) growth temperature, (2) reactor pressure, (3) VI/II molar ratio, (4) substrate baking procedure, and (5) ratio of gas velocities in the carrier gas to MO lines. To grow a high quality film with good morphology, the epilayer should be of uniform thickness. The main parameter that affects the uniformity of the epilayer thickness was found to be the ratio of gas velocities in the carrier gas to MO lines. In varying this ratio from 0.2 - 10.6, epilayers of uniform thickness were observed from 7.3 to 8.7. The uniformity was maintained in this range regardless of the growth temperature which was varied from 250 to 450°C. Apparently, natural convection of reactant gases does not greatly affect the thickness uniformity.

The growth process is usually better controlled if it is mass transfer limited rather than kinetically limited. Measurement of the growth rate as a function of temperature showed that the ZnCdS

growth was constant in the temperature range 300 to 450°C. This indicates that the growth process is mass transfer limited at these temperatures. In the mass transfer limited region, the growth rates for the (100) +/- 0.5° and the (100) 2° GaAs substrate were 5.5 μm/hr and 6.8 μm/hr, respectively. The conditions for these runs were: reactor pressure = 70 Torr, VI/II = 117, [DMCd] = 42.8 mmol/min, and [DEZn] = 28.6 mmol/min.

At 400°C with mass transfer limit, the growth rate was measured as a function of the molar flowrate of DMCd + DEZn. Since the VI/II ratio was always much greater than one, the organometallics were the limiting reactants at these growth conditions. As expected, a linear relationship between growth rate and group II molar flowrate was observed.

To better understand and better control the growth process, the solid composition of $Zn_{1-x}Cd_xS$ was measured as a function of growth temperature. The incorporation of Cd into solid ZnCdS varied with growth temperature. The results showed that the film was Cd-rich at growth temperature in the range 250 to 450°C. As the temperature approached 450°C, the solid composition nearly matched the inlet mole fraction. For a gaseous Cd composition of 0.6 ([DMCd]/{[DMCd] + [DEZn]} = 0.6), the solid composition of Cd (x of $Zn_{1-x}Cd_xS$) at 250 and 450°C was 0.715 and 0.645, respectively. The data showed an exponential decay between these two bounds. In the lower temperature range, ZnCdS was Cd-rich, possibly because the DEZn had not fully decomposed. In addition, the sticking coefficient could be higher at lower temperatures for Cd, thereby producing a Cd-rich epilayer. More studies need to be performed to determine the reasons for this behavior.

The lattice constant of $Zn_{1-x}Cd_xS$ was determined as a function of solid composition (EMPA) for the first time. The data indicates that Vegard's Law is followed, assuming that the binary materials of ZnS and CdS have the cubic structures. The FWHM of X-ray diffraction peaks is one of the measures of the quality of the epilayer. A plot of the FWHM versus solid composition showed a local minima where ZnCdS is lattice-matched to GaAs at the solid composition of x = 0.58. The FWHM at the lattice matching conditions is approximately 2000 arc-seconds. Preliminary photoluminescence data for this lattice matched composition indicates that the maximum peak is near 2.85 eV at 18 K. Although the luminescence position does not reflect the expected bandgap energy, its near-bandgap energy suggests that ZnCdS is a viable candidate for blue-light emitting optoelectronic devices.

Of the five growth parameters examined, the baking procedure was the most important to the quality of the surface morphology. Baking temperature was the most important parameter in the production of consistently smooth epilayers. At 550°C, about half the films were smooth. At 600 to 750°C, the films always showed good morphology. The baking times were varied from 10 to 20 minutes. The optimal baking condition was at a temperature of 620°C, pressure of 50 Torr and a time of 15 minutes.

The growth pressure was found to not be an important factor in

determining the film properties. The crystallinity also was independent of the VI/II ratio as long as the ratio was much greater than one.

(II.2) Nitrogen prebonded precursors to dope ZnSe: Progress was also made in the development of prebonded Zn-N precursors for p-type doping of Zn-based films. This work is being performed in collaboration with Dr. W. Rees at Florida State University. Four new precursors have been synthesized and screened as possible candidates. These precursors involve two nitrogen atoms bonded to a central Zn atom and three ligands ($Si(CH)_3$, C_3H_7, or C_4H_9) bonded to each N atom. Mass spectroscopic decomposition studies and vapor pressure measurements indicate two of these precursors merit further investigation.

(III) Ohmic contact formation (Paul Holloway)

Formation of ohmic contacts to p-ZnSe doped to > 3 x 10^{17} cm^{-3} with N has been attempted using a number of evaporated and sputter-deposited metals. The electrical characteristics (I-V) of the contact was studied as-deposited or after heat treatment in a forming gas environment at temperatures up to 400°C. Evaporated metals studied include Au, In, Sn, and In-Sn alloys. Sputter-deposited metals include Au, Ag, Cu and Ag-Cu alloys. In every instance, the as-deposited contacts were rectifying with very low currents (≈ nanoamps) and high breakdown voltages (> 5V). Annealing reduced the breakdown voltages of most metals, however the reduction of that of Au was the greatest and it reached minima of ≈ 4V after heating to >200°C for times ≈ 30min. Even with the reduced breakdown voltages, the currents were still very low and the contacts were very rectifying. Above a temperature of about 350°C, the resistance of the ZnSe itself increased and the I-V curves for the contacts often appeared to be linear; this resulted not from formation of ohmic contacts, but because $R_{ZnSe} \approx R_{contacts}$. We have concluded that metals and alloys to form ohmic contacts is unlikely to be fruitful for ohmic contacts to p-ZnSe.

As a result we have turned our attention to evaporation of semiconductors onto the epilayers. We have evaporated the elemental semiconductors Se and Te onto the p-ZnSe and studied the I-V characteristics both as-deposited and after heat treatment. Again the as-deposited films are rectifying, but the breakdown voltage for Te heat treated to ≈ 150°C was reduced to ≈ 2V with currents near the mA range. This led us to speculate that we could form HgSe contacts similar to Schetzina, et al [Appl. Phys. Lett. **61** (1992) 2554] by evaporating the Se layer and reacting with Hg vapors in a hood. This idea has been carried one stop further by capping the p-ZnSe with a Se layer at the end of the MBE growth. This cap will prevent interfacial contamination of the p-ZnSe and still allow ex situ formation of HgSe or other semiconductor contacts. We have formed HgSe contacts ex situ using this approach and found the growth of the contact to be diffusion limited for Se

layers ≈ 3000Å thick. The reaction proceeds at reasonable rates at temperatures near 150°C over times of 15-500 min. The HgSe formed is conductive, however the breakdown voltages for the contacts still remains near ≈ 1.5-2V. We believe this results from an excess Se layer near the interface, and are exploring higher reaction temperatures, longer times, and thinner Se layers to rectify the problem. We also feel that incorporation of Te in the capping layer will improve the results. Based on the success of capping the ZnSe surface prior to formation of the ohmic contact, we speculated that capping the surface of n-GaAs with a sulfur-passivation layer would lead to easy formation of ohmic contacts. To test this hypothesis, we used an aqueous ammonium sulfide solution to remove the native oxide layer and replace it with a sulfide layer bound to the Ga and As [Y. Wang, P.H. Holloway and Y. Darici, J. Appl. Phys. **71** (1992) 2146] to avoid reformation of the native oxide. The S layer was thermally desorbed in UHV and a Au film deposited onto the surface without exposure to vacuum. The I-V characteristics of the Au contacts as deposited showed they were good ohmic contacts. Subsequent SIMS and C-V analyses showed that the surface region of the GaAs wafer was doped n^+ by the S, and this explain the formation of a sinter-less ohmic contact. A manuscript describing this work is in preparation and will be submitted shortly.

We believe that the general approach of capping and passivation prior to formation of ohmic contacts may be a very important area in future development of ohmic contacts for compound semiconductors, including ZnSe and the column III nitrides.

(IV) Microstructural characterization of column III nitride films (Kevin Jones)

The III-V nitrides - GaN, AlN and InN - form a continuous alloy system with direct bandgaps ranging from 1.9eV for InN to 3.4eV for GaN to 6.2eV for AlN. Thus the III-V nitrides could potentially be fabricated into optical devices which are active at wavelengths ranging from the red well into the ultraviolet. In addition, the large bandgaps make these semiconductors excellent prospects for high temperature microelectronic devices.

We have initiated work on nitride thin films in collaboration with Drs. K. Abernathy, A. Katz and S.J. Pearton at AT&T Bell Laboratories in Murray Hill, NJ, in addition to examining films grown at the University of Florida (see above). Dr. Abernathy is growing III-V nitrides in an MBE modified with a RF nitrogen source. To date, films of AlN, GaN and InN have been grown on InP, sapphire and GaAs substrates. The goal is to grow high quality single crystal films (both hexagonal and cubic structures are being investigated) with a stoichiometry suitable for doping. Results of our characterization of these films are summarized below.

(IV.1) <u>AlN, GaN and InN layers grown on (001) InP</u> The structural characterization of these films was carried out at the University

of Florida and electrical characterization at AT&T Bell Laboratories (Drs. Katz and Pearton). X-ray and transmission electron diffraction results indicate the films are highly oriented. The hexagonal basal plane (0001) of AlN, GaN or InN is parallel to the (001) surface of the InP substrate. Plan view and cross-sectional TEM diffraction data indicate that the films are polycrystalline with columnar grains. The diameter of the grains was 100-200Å for AlN, 300-500Å for GaN and 1000-1200Å for InN. The samples were subsequently annealed for 30 minutes at temperatures between 300 and 600°C. There was no significant difference in crystal structure between the as-deposited versus annealed samples. This experiment indicates that III-V nitride films can be grown in MBE systems.

(IV.2) AlN and GaN layers grown on (0001) sapphire and (001) GaAs A second series of samples were grown in order to explore methods of growing hexagonal and cubic single crystal films. The samples received from AT&T for structural characterization are listed below:

20813-1	AlN on sapphire
20813-2	GaN on sapphire
20921-1	GaN on sapphire / AlN buffer
21022-1	GaN on sapphire / low T buffer
21103-3	GaN on GaAs

AlN has a lattice constant of a = 3.112Å. This is closer to the lattice constant of GaN, a = 3.189Å, than sapphire, a = 4.758Å. Thus an AlN buffer layer is expected to improve the crystallography and morphology of GaN grown on sapphire by grading the mismatch. It has been demonstrated that it is possible to grow high quality GaN layers on a strained low temperature buffer layer. The epitaxial growth on this low temperature buffer layer is expected to lead to good quality single-crystalline β-GaN (cubic) with a smooth surface morphology.

Initial results from X-ray diffraction indicate that the samples could be single crystal. Because of the strong tendency of the basal plane to orient itself parallel to the surface, it is not possible by X-ray alone to determine if the films are truly single crystal. SEM analysis and cross-sectional TEM studies are in progress to determine whether single crystal films have been grown. TEM data will also reveal the defect densities. Electrical measurements are in progress at AT&T Murray Hill.

(V) Optical characterization of ZnSe (Joe Simmons)

(V.1) PL measurements on novel materials We have conduced a variety of PL measurements at 10-12°K on undoped, n-type and p-type doped ZnSe. The results, depicted in Figs. 1-3, show the presence of free and bound excitons in undoped and p-type ZnSe. The dominant feature in both films is the donor-acceptor pair transition, showing the relatively high compensation encountered in the doped

films. Measurements on the n-type film show a band edge emission and a comparatively weak deep level emission indicating the high structural and optical quality of the fabricated films.

(V.2) Time resolved PL studies We have ordered and received delivery on both short pulse emission and detection instruments. The emission will be achieved through a frequency-doubled 200fs Ti-sapphire laser, to be installed before the end of January. The detection equipment consists of a fast diode-boxcar integrator system with a 12GHz digital scope for nanosecond-scale studies. First measurements are anticipated in quantum well structures in February.

(VI) Analytical modeling of the carrier concentration and mobility in doped ZnSe films (Joe Simmons)

A numerical approach for calculating the full solution to the Boltzman Equation was modified to apply to ZnSe. This approach calculates the full carrier and impurity screening contributions, generally ignored by other investigators, which are, however, essential at high dopant concentrations. Preliminary studies find an excellent agreement between modeled functions and measured concentration and mobility by Hall effect in n-type ZnSe films. The n-ZnSe was grown and carrier characteristics were measured by Robert Park and Chris Rouleau. The numerical approach has given us insight into the nature of the semiconductor-metal transition which is observed in these films. Specifically, the numerical approach indicates two donors exist in n-ZnSe, one below (≈12 meV) and one above (≈10 meV) the bottom of the conduction band. The concentration of donors are a function of doping density, being dominated by the donor below the bottom of the conduction band. Our estimates of the exact energies and concentration of donors is currently being refined by final fitting procedures. A comprehensive report of the study will be prepared shortly.

(VII) Photopumping to test quality of material for lasing by electrical injection (Peter Zory)

(VII.1) Photopumping of ZnSe MOCVD epilayers A number of ZnSe epitaxial films of different thickness were grown on GaAs substrates by MOCVD (B. Pathengy and T.J. Anderson). Photopumped lasing experiments were carried out, the data analyzed and the results summarized in a paper to be submitted for publication. A strong dependence of the laser threshold pump intensity (I_{th}) on pump photon energy ($h\nu$) and film thickness (t) was found and successfully modeled. The main conclusion is that the experimenter must understand how to properly select t and $h\nu$ in order to accurately utilize I_{th} as a measure of the potential of such films to be used as active layers in electrically injected diode light emitting devices.

(VII.2) Photopumped lasing of CdZnSe/ZnSe MQW structures
Photopumped lasing was achieved in CdZnSe/ZeSe multiquantum well (MQW) material grown by MBE (L. Calhoun and R.M. Park). Threshold pump intensities as low as 35 Kw/cm^2 were found for devices made with 100 μm by 500 μm cavities (work done by F. Ihren under the supervision of Y. Guan and P. Zory). This value compares favorably with the best data reported in the literature for such structures. Far field measurements were made and used to determine the effective refractive index difference Δn between the MQW active layer and the ZnSe cladding layers. The result, Δn = 0.09 for beam divergence of 33°, combined with the low threshold pump intensity indicates that this structure has good potential for making guasi-DH diode lasers, provided good injection efficiency into the MQW active region and degradation resistance can be achieved. Photopumped lasing over several hours did not produce any noticeable degradation, although the duty cycles used were quite small. A master's degree thesis summarizing these results has been completed.

(VIII) Strained Quantum Well Laser Theory (Peter Zory)

The fundamental relationship between peak optical gain, g, and current density, J (the g vs J relation), for strained CdZnSe quantum well/ZnSe laser configurations has been derived assuming strict k-selection and valence band mixing (work done by Y. S. Park, G. Lim and P. Zory). This relation allows one to predict the temperature dependence of threshold current density of diode lasers incorporating such structures. Since the results of the calculation are in disagreement with published theoretical work, a paper is being written discussing the disagreement. We intend to use this theoretical work to predict the temperature dependence of the visible emission properties of blue-green diode laser structures. These predictions will be compared with experiment. We believe that a thorough understanding of the temperature dependence of light emission from such devices will lead ultimately to improved designs capable of operating cw at room temperature.

(IX) SUBCONTRACT TO COLUMBIA UNIVERSITY (Gertrude Neumark)

Theoretical Calculations for Dopants in ZnSe

We are trying to understand differences in predicted acceptor solubilities, of three to four orders-of-magnitude, between first-principles calculations by Dr. Van de Walle and our thermodynamic analysis. Based on the first-principles results, it should be possible to obtain adequate impurity incorporation (about 10^{19}/cm^3 for N) by equilibrium means; our thermodynamic results lead to the conclusion that non-equilibrium incorporation is essential.

We have discussed this problem extensively with Dr. Van de Walle. We now both agree that if his calculated defect energies

are off by 0.3 to 0.4 eV, then both calculations could give consistent solubility values; however, he believes his values are good to at least 0.2 eV, and probably closer to 0.1 eV. For the method of mixed basis sets used by Van de Walle, which is the best theoretical method presently available, obtaining improved error limits is a formidable task. This is particularly true for the impurity of main present interest, N, which has a very strong potential. We thus felt it would be better, for the time being, to:

1) Calculate solubility values as a function of defect energies, i.e. determine quantitatively how large an error in defect formation energies would be required to give solubilities consistent with the thermodynamic analysis. We have started writing the appropriate program.

2) Carry out a search of the literature to find data which, with re-analysis if required, indicates whether, experimentally, incorporation appears to be equilibrium or non-equilibrium. Such a re-analysis has already been done on one paper [Haase et al., J. Appl. Phys. 67, 448 (1990)]. It indicated that equilibrium incorporation was appreciably lower than the first-principles results.

So far, in the literature search, we have noted the paper by Qiu et al., [Appl. Phys. Lett. 59, 2992 (1991)], which shows that, at high N concentrations, values from SIMS are appreciably higher than the active dopant concentrations. Thus a good part of the N is present in some non-dopant form; this strongly suggests low N solubilities. A further point of interest in connection with the literature survey relates to work on n-ZnSe. Various evidence for low dopant solubilities in this case has been summarized by us earlier (G.F. Neumark, in "Widegap II-VI-Compounds for Opto-electronic Applications", p. 280, Chapman & Hall, 1992). However, it is worth mentioning that a puzzling result was obtained by Jones and Woods [J. Phys. D 9, 799 (1976)], namely that the carrier concentration actually decreased (at high dopant levels) with increasing (Ga) dopant concentrations. We have now, in our literature search, found an article which can explain this: Skudlarski and Pawlikowski [Sol. St. Comm. 60, 111 (1986)] suggest that with increasing dopant concentrations one forms a higher concentration of second-phase precipitates, which in turn enable more of the dopant to precipitates out (i.e. with the dopant thus better able to reach its equilibrium solubility instead of remaining in a super-saturated state). Work in this area will continue.

(X) SUBCONTRACT TO OREGON GRADUATE INSTITUTE OF SCIENCE AND TECHNOLOGY (Reinhart Engelmann)

Gain Modelling in II-VI Strained-Layer QW Structures

The investigation during this quarter was mainly concentrated

on the search for new laser structures with improved carrier confinement and, hence, optical gain. To this end the possibilities of increasing the bandgap of II-VI alloys was explored by incorporation of IIa elements, such as Mg and Ca. Two systems are discussed, the ZnCaCdS system lattice matched to GaAs and the ZnMgSeTe system lattice matched to CdSe (or InAs). Additionally, important issues, such as the doping and ohmic contact problem were considered in choosing new cladding materials based on the ZnMgSeTe quaternary alloy system.

Ternaries (or quaternaries) involving hypothetical (metastable) zincblende II-VI binaries (involving Be, Mg, Ca, etc.) would open up the available energy range for laser design. Properties of BeTe, BeSe, and BeS have been investigated in the past [1], and it was shown that all of these Be compounds have indirect bandgaps. Mg had been introduced already 25 years ago to obtain shorter wavelengths for light emitting diodes [2,3]. Recently, Okuyama et al have proposed using ZnMgSSe as a cladding layer material [4], and achieved continuous operation of a ZnSe/ZnMgSSe blue laser diode at 77 K [5]. CaS, SrS and BaS have attracted much attention as host materials in the preparation of industrial phosphors [6] , but no efforts have been directed towards their incorporation into II-VI ternaries or quaternaries for blue/green diode lasers.

In this report, we first describe a laser structure based on the ZaMgSeTe system on which sufficient data are available from related earlier work. Then we introduce another structure made from ZnSe/ZnCdCaS/ZnCdS which, however, leaves some questions still open at this time.

(X.1) Design considerations of ZnMgSeTe diode lasers There are many obstacles in decreasing the value of laser thresholds and yielding a cw room temperature injection diode laser. The most significant ones are the inability to dope high bandgap II-VI materials both p-type and n-type (amphoteric doping), the lack of lattice matched heterostructures with good carrier confinement, and poor ohmic contacts. Based on our theoretical analysis, we concluded that by introducing the new quaternary alloy ZnMgSeTe, progress in solving these difficulties are very likely to be achieved.

All II-VI compounds with energy gaps in excess of 2 eV are unfortunately subject to strong compensation effects because of the partial ionic character in the bond type. Some of them (ZnSe, CdSe etc.) are found to be primarily n-type while others (ZnTe) are only p-type. Doping of ZnSe has been extensively studied, and a breakthrough in p-doping has been demonstrated by applying the nitrogen radical doping technique [7], which led Haase et al.[8] to successfully fabricate the first blue-green laser diode operating at 77 K. While further improvements of these devices are still expected, reliable room temperature CW operation is still lacking. An alternate way to overcome this doping problem is to mix the selenides with tellurides [9-12]. It was found that ZnTe is the only binary of the wide bandgap II-VI semiconductors which has a

p-type residual conductivity, and that the $ZnSe_yTe_{1-y}$ alloy can be doped both p-type and n-type in the composition range of $0.4<y<0.6$ [9]. Good quality ZnSeTe material has been grown by MBE [10,11] and MOCVD [12] on various substrates (GaAs, InP, InAs, and ZnTe). Due to the large bowing parameter, the band gap of $ZnSe_yTe_{1-y}$ close to y = 0.4 has a lowest value of only about 2.2 eV. Additionally, ZnTe/ZnSe heterostructures have been found to be of type II alignment. This makes $ZnSe_xTe_{1-y}$ less attractive than ZnSe and ZnSSe for blue/green light emitting diode lasers.

For better carrier confinement, a large band gap difference (>0.3 eV) between active and cladding layers is desirable. Also, it is important that the band offset be shared more evenly between the conduction and valence bands. As discussed previously, it is very hard to satisfy these conditions in standard lattice matched II-VI heterostructures. The ohmic contacts p-type ZnSe and related alloys is a fundamental problem that arises as a consequence of the large potential barrier for holes between a metal (or GaAs) and ZnSe.

All of the above problems could possibly be solved by introducing a new diode laser structure based on ZnMgSeTe quaternary alloys. The basic idea is to take advantage of the possibility of amphoteric doping in ZnSeTe and add Mg to increase the bandgap energy. The bandgap energy and lattice constant of quaternary $Zn_{1-x}Mg_xSe_yTe_{1-y}$ alloys vary from 2.2 to 3.6 eV and from 5.66 to 6.28Å, respectively (Fig. 4.). So by choosing the appropriate quaternary composition of the ZnMgSeTe alloy for both active and cladding layers at a fixed lattice constant, good heterostructure designs for diodes lasing in the range of yellow, green and blue are expected.

(X.2) <u>ZnMgSeTe diode laser structure</u> The bandgap energy vs. lattice constant diagram of high bandgap II-VI zincblende-type binaries related to the ZnMgSeTe alloy system is shown in Fig. 4. Most of the data are taken from [14] except those for MgS and MgSe which are taken from [10], and the data for MgTe which are estimated from [2]. The data of the ternary alloys are also shown. Notice that $MgSe_{1-y}Te_y$ has a similar bowing characteristic as does $ZnSe_{1-y}Te_y$. Hence, we could also expect that these ternaries, as well as the corresponding quaternaries (along the dotted tieline in Fig. 4), have a similar amphoteric doping property.

For the cladding layers, the Te mole fraction y of $Zn_{1-x}Mg_xSe_{1-y}Te_y$ should be in the range of 0.4 - 0.6 in order to get both p-type and n-type doping. To insure good carrier confinement, the band gap of the cladding should be close to 3 eV for blue light emission. So a high Mg mole fraction x (about 0.7 from Fig. 4) is needed in this case. Several lattice matched substrates are possible for this composition, such as InAs, GaSb, HgSe, and CdSe. In view of the ohmic contact problem, lattice matching to InAs or HgSe, possibly with a CdSe transition layer, seems a preferred choice [15]. With these considerations we propose $Zn_{0.3}Mg_{0.7}Se_{0.4}Te_{0.6}$ as cladding layer material, which we call ZnMgSeTe I.

For the active layer, the band offset is the most important

issue. It is the advantage in our proposed ZnMgSeTe system that the Se/Te ratio can be adjusted to provide reduced valence band offset thus overcoming the type II alignment problem of the ZnSe/ZnTe system. Considering for the time being only the unstrained case, the active layer material would be $Zn_{0.7}Mg_{0.3}Se_{0.2}Te_{0.8}$, which we call ZnMgSeTe II. In summary, our proposed new DH diode laser structures is shown in Fig. 5.

Additional remarks regarding the expected crystal structure appears to be appropriate. Pure MgSe tends to crystallize in the rock salt structure. It was recently argued that MgTe's stable configuration should be of the NiAs type, but that two possible metastable forms, zincblende and wurtzite, may exist with zincblende being preferred [13]. MgSe also has a metastable zincblende structure. Furthermore it is likely that the metastable forms can be stabilized during growth [13]. The recent success in growing the ZnMgSSe system in the zincblende form [5] leads us to believe that the growth of our proposed hypothetical ZnMgSeTe quaternary alloy in that same crystal structure should not pose a problem. The pure MgTe crystals are extremely hygroscopic. In contact with the atmosphere, they are immediately hydrolyzed. MgSe is also unstable when exposed to the atmosphere. Hence, with Mg-containing alloys, a capping layer is needed to protect the surface.

(X.3) Other structures based on CaZnS Besides Mg, Ca might be another choice of group IIa, to give more flexibility for DH structure design. We are not aware of any work on zincblende structures that contain Ca. We estimate the bandgap and lattice constant of zincblende CaS based on the rock salt structure data of CaS and MgS, and propose a new ZnSe QW laser structure based on the ZnCaCdS quaternary alloy system lattice matched to GaAs as shown in Fig. 6. The advantage of this system would be a better composition control during growth since only one VI constituent is required. Additionally, the system could be adjusted to provide lattice matching to commercial GaAsP epi-material, thereby allowing for larger bandgaps in the active QW layer by incorporation of S into ZnSe to form a ZnSSe QW. This could provide an extension of the available wavelength range into the ultraviolet. The p-type doping of the proposed quaternary alloys, on the other hand, remains an open question.

(X.4) Discussion and conclusion Using a ZnMgSeTe quaternary alloy provides several advantages for II-VI diode lasers, such as the possibility for high doping of both p-type and n-type, and large band offsets in both conduction and valence bands with lattice matched active and cladding layers. All these advantages are dependent on very accurate control of the composition of each epitaxial layer. Hence, investigations on the growth conditions for these compounds need to be done in the future, both experimentally (by MBE and MOCVD) and theoretically. Growth simulations in such a system become more important, since a higher degree of complexity is involved compared to III-V systems.

In conclusions, we have proposed new diode laser structures based on ZnMgSeTe and ZnCaCdS quaternary alloy systems. The basic idea for the ZnMgSeTe system is to take advantage of the possibility of amphoteric doping in ZnSeTe and add Mg to increase the bandgap energy. By using $Zn_{0.7}Mg_{0.3}Se_{0.8}Te_{0.2}$ as the active layer and $Zn_{0.3}Mg_{0.7}Te_{0.6}Se_{0.4}$ as cladding, a DH structure can be designed to improve diode laser performance for light emission at green-blue wavelengths.

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(XI) SUBCONTRACT TO UNIVERSITY OF COLORADO (Jacques Pankove)

MOCVD Growth of Column III Nitrides

We grew a number of GaN layers on (1102) sapphire and on Si. Their yellow color suggests the presence of oxygen. These samples are conducting. Samples were examined by SEM, as shown in Fig. 7. During our investigation, several parameters were varied. Eventually, no growth was obtained. This was traced to the exhaustion of the TEG source. We have devised techniques for assaying the exhaustion of TEG by using our residual gas analyzer to look for Ga after the end of each run.

Some insulating GaN layers were grown. Carbon from TEG is expected to form a deep acceptor and could result in insulating films. SIMS analysis showed that the material contains approximately 10^{18} cm^{-3} O and C. Samples grown in the system before cleaning the As from earlier GaAs depositions also contained As. Optical transmission measurements to find a deep level that might be responsible for the yellow to brownish color of the GaN layer indicated the onset of strong optical absorption at photon energies of 3.1 eV. This would be consistent with the presence of oxygen as suggested above.

We have been able to again produce conducting GaN on sapphire and have attributed the recovery of conductivity to the procedure used of gradually bring the substrate up to deposition temperature. We have observed that gradual heating produces a film on the substrates that appears at 300 to 400 °C and disappears when NH_3 is introduced. This film may be a necessary precursor to the growth of conducting GaN.

An attempt to grow GaN by microwave plasma-assisted MOCVD resulted in a Ga coating, while an attempt to grow GaN under ECR conditions resulted in a coating of soot. Obviously these two

techniques need refinement. This will be done after obtaining satisfactory GaN by low-pressure MOCVD.

The geometry of gas flow was modified by bringing NH_3 and TEG closer to the substrate and by inserting a baffle to move the exhaust past the substrate instead of under it (Figure 8). This caused the decomposition of TEG inside the shower head, now radiation-heated by the nearby hot substrate. Hence, there was no transport of Ga to the substrate.

Other changes to the deposition chamber are underway to solve this and other problems. These include

-fabrication of a graphite substrate holder (the tantalum holder deformed and cracked);

-fabrication of a larger front plate with 8" conflat gasket to permit easier access inside chamber for cleaning and changing positions of NH_3 nozzle and TEG shower head;

-installation of feed-throughs to bias substrate and grid during ion-beam deposition and to energize a hot wire for more efficient cracking of NH_3.

Basal plane sapphire was purchased. A spare supply of TEG was ordered (exceeding our budget). We shall also ordered a Millipore filter to block O_2, H_2O and NH_4OH from the NH_3 line. We have obtained access to a clean room with substrate cleaning facilities. We intend to use these facilities to improve the substrate surface cleanliness and eliminate any coloration of the GaN films that might be due to residues left on the substrate as a result of the old cleaning methods.

Publications

1. "Photopumped Lasing of Variable Thickness ZnSe Thin Films" by Y. Guan, P. S. Zory, B. Pathangy and T. J. Anderson to be submitted for publication.

2. "Photopumped ZnSe/CdZnSe MQW Lasers" by F. Ihren, Master of Science Thesis, Dept. of Electrical Engineering, University of Florida, December, 1992.

3. "GaAs substrate cleaning for epitaxy using a remotely generated atomic hydrogen beam", by C.M. Rouleau and R.M. Park, J. Applied Phys., in press.

4. "Formation of ohmic contacts on n-GaAs using $(NH_4)_2S$ surface passivation", V. Fischer, P.H. Holloway, E. Ristolainen and D. Schoenfeld, to be submitted.

5. "Electrical Properties of n-Type ZnSe/GaAs Epilayers Deduced from Optical (Near-infrared) and dc Hall-effect Measurements: A Comparative Study", A. Deneuville, V. Zelezny, D.B. Tanner, C.M. Rouleau, R.M. Park, and P.H. Holloway, to be submitted.

6. "Indium Ohmic Contacts to n-ZnSe", Y.-X. Wang and Paul H. Holloway, Vacuum **43**, 1149 (1992).

7. "Growth of GaN, InN and AlN by ECR MOMBE", P.W. Wisk, C.R. Abernathy, S.J. Pearton, F. Ren, J.R. Lothian, A. Katz, K.S. Jones, D.A. Bohling and W.S. Hobson, Proc. MRS Fall 1992 Symposium, in press.

8. "Electron Microscopy of Post-Growth Induced Defects in ZnSe/GaAs Epilayers", J.E. Yu and K.S. Jones, J. Electronic Mater. **22**, 239 (1993).

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10. "Spectral Dependence of Differential Gain, Mode Shift and Linewidth Enhancement Factor in InGaAs/GaAs Strained Layer Single-Quantum-Well Laser Operated under High Injection Conditions", R. Raghuraman, N. Yu, R. Engelmann, H. Lee and C.L. Shieh, IEEE J. Quantum Electronics **QE 29**, 69 (1993).

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12. "Proposed Novel Blue-Green Laser Diode based on ZnMgSeTe Alloy System", Y. Cai and R. Engelmann, to be published.

13. "Threshold Current Density of CdZnSe/ZnSe Strained Single Quantum Well Diode Lasers", Y. Park, P.S. Zory and G. Lim, to be submitted.

Presentations

1. G. Neumark and R. Park will both give invited talks at the March 1993 meeting of the American Physical Society on doping and growth of ZnSe based materials and lasers.

2. C. Rouleau and R. Park, "In situ, real time monitoring of ZnSe/GaAs thin film parameters during molecular beam epitaxial growth", 39th National Symposium of the American Vacuum Society, Chicago, Nov. 9-13, 1992.

3. H.F. Arlinghaus, M.T. Spaar, N. Thonnard, P. H. Holloway, A.C. Diebold and P. Maillot, "Quantitative and sensitive profiling of dopants and impurities in semiconductors using sputter initiated resonance ionization spectroscopy (SIRIS)", ibid.

4. Y. Darici, J. Marconi, D. Wu, V. Fischer and P.H. Holloway, "Thermal desorption of passivating sulfur from GaAs", ibid.

5. "The Formation of Ohmic Contacts to GaAs", Paul H. Holloway, Invited Paper, XII National Congress of the Mexican Vacuum Society, Cancun, Sept. 22, 1992.

6. "Epitaxial Growth of Compound Semiconductor", Paul H. Holloway, Invited Short Course/Tutorial Lecture, XII National Congress of the Mexican Vacuum Society, Cancun, Sept. 21, 1992.

7. "Chemical Reactions at the Au/GaAs Interface", P.H. Holloway, Invited Seminar, Tampare University of Technology, Tampare, Finland, Oct. 5, 1992.

8. "MOCVD Growth of ZnS Electroluminescent Thin Films", P.H. Holloway, Invited Seminar, Planar Intl. Oy, Espoo, Finland, Oct. 6, 1992; also Helsinki University of Technology, Espoo, Finland, Oct. 7, 1992.

9. "Analysis of Solid Surfaces", P.H. Holloway, Invited Seminar, University of Helsinki, Helsinki, Finland, Oct. 8, 1992.

10. "Metal-MBE Grown ZnSe Interface and Ohmic Contacts", Y.-X. Wang and Paul H. Holloway, National Conference on Condensed Matter Physics, Beijing, PRC, October, 1992.

11. "Growth of GaN, AlN and InN by Metalorganic Molecular Beam

Epitaxy using ECR Generated Nitrogen Plasmas", P.W. Wisk, C.R. Abernathy, S.J. Pearton, A. Katz, F. Ren and K.S. Jones, 1992 Fall MRS Meeting, Nov. 30-Dec. 3, 1992, Boston.

12. "Microstructure of ZnS Layers Grown by MOCVD for Thin Film Electroluminescent Displays", J.E. Yu, K.S. Jones, T. Anderson and P.H. Holloway, Florida Chapter of Scanning Electron Microscopy Society, 10th Annual Meeting, Crystal River, FL, Aug. 1992.

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14. "Wavelength Switching in Quantum Well Lasers at High Injection", R. Engelmann, Invited Seminar presented at:
    Wright Laboratories, WPAFB, OH, July 27 1992.
    David Sarnoff Research Center, Princeton, NJ, July 28, 1992.
    US Army Electron Devices and Technology Laboratory, Ft. Monmouth, NJ, July 29, 1992.
    Dept. of Electrical Engineering, Univ. of Florida, Gainesville, FL, Aug. 3, 1992.
    Dept. of Electrical Engineering, Portland State Univ., Portland, OR, Nov. 13, 1992.

15. "Dual Wavelength Laser Operation in Lossy Gain-Guided InGaAs/GaAs Strain-Layer Quantum Well Laser Stripe", R. Raghuraman, R. Engelmann and J.R. Arthur, 1992 OSA Annual Meeting, Albuquerque, NM, Sept. 20-25, 1992.

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17. "Status of Research on Blue Emitters", Jacques Pankove, Invited Lecture, French and American Midwestern Workshop on III-V and II-VI Semiconductor Compounds, Chicago, IL, Oct. 9, 1992.

Graduate Research Assistants Supported by URI

1. John Fijol and Jeff Trexler with Paul Holloway

2. Sushil Bharaton with Kevin Jones

3. Li Wang with Joe Simmons

4. Bruce Liu and Austin Frenkel with Robert Park

5. Eric Brettschneider and Joe Cho with Tim Anderson

6. Young-soh Park and Chi-lin Young with Peter Zory

7. Y. Cai with R. Engelmann

8. William A. Melton with Jacques Pankove

Undergraduate Research Assistants Supported by URI

1. Bob Covington with Tim Anderson

2. Greg Darby with Paul Holloway

Post-Doctoral Associates

1. Dr. Y. Guan and Dr. Y.S. Park, Dept. of Electrical Engineering, University of Florida, with Peter Zory

2. Dr. Chris Walker (0.5 FTE), Dept. of Electrical Engineering, University of Colorado, with Jacques Pankove (thru 1/31/93).

3. Dr. Wafaa Golsba, Dept. of Materials Science and Engineering, University of Florida, with Joe Simmons.

Low Temperature PL of ZnSe Sample 1038

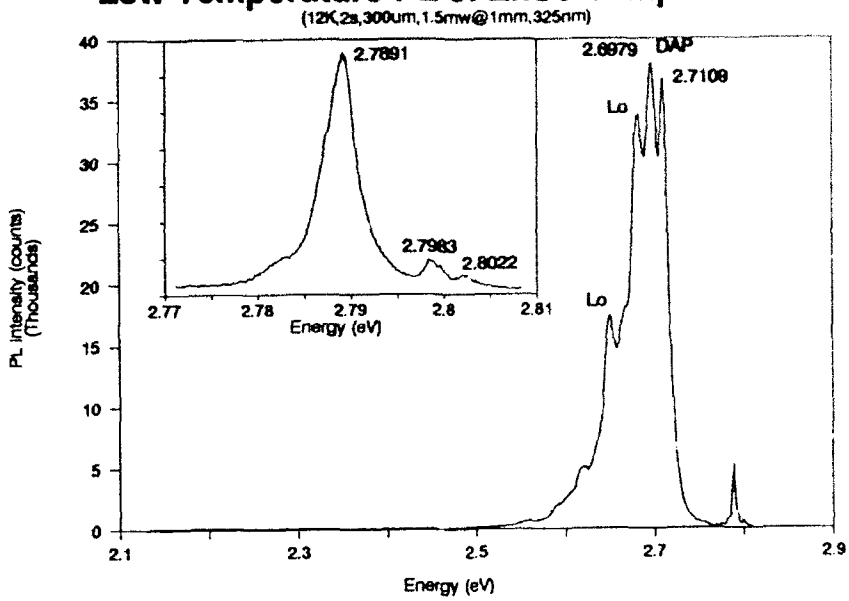
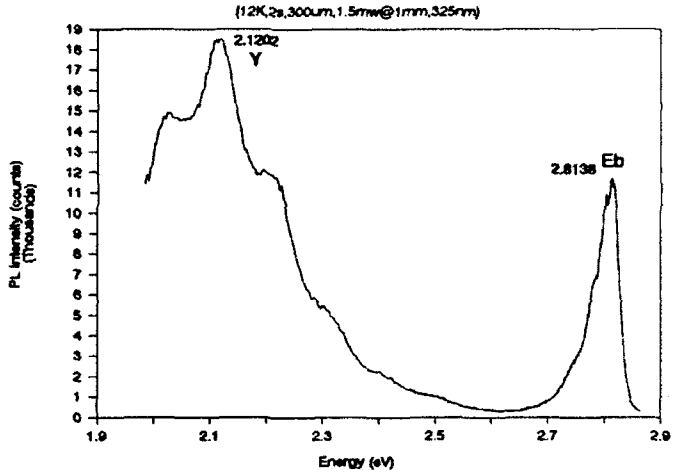


Fig. 1

Low Temperature PL of ZnSe Sample 1057 (n-type)

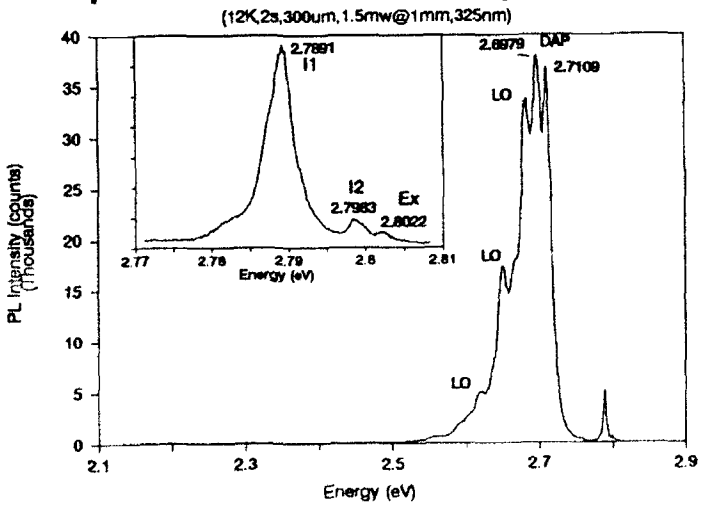


Eb- band edge emission

Y- deep level emission

Fig. 2

Low Temperature PL of ZnSe Sample 1038 (p type)



Ex- free exiton emission

I1- acceptor bound exiton emission

I2- donor bound exiton emission

DAP- donor acceptor pair emission

LO- longitudinal phonon replica

Fig. 3

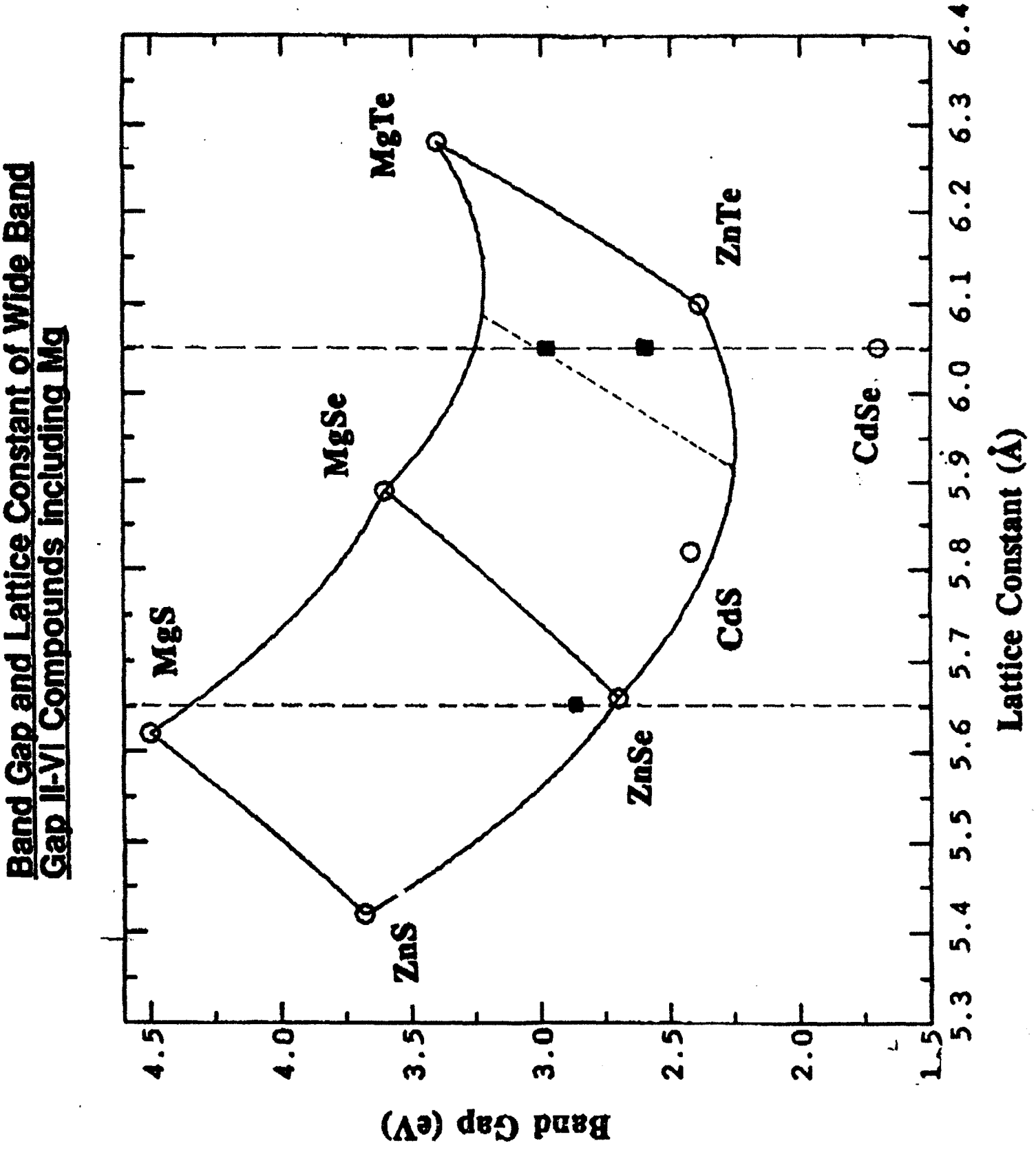
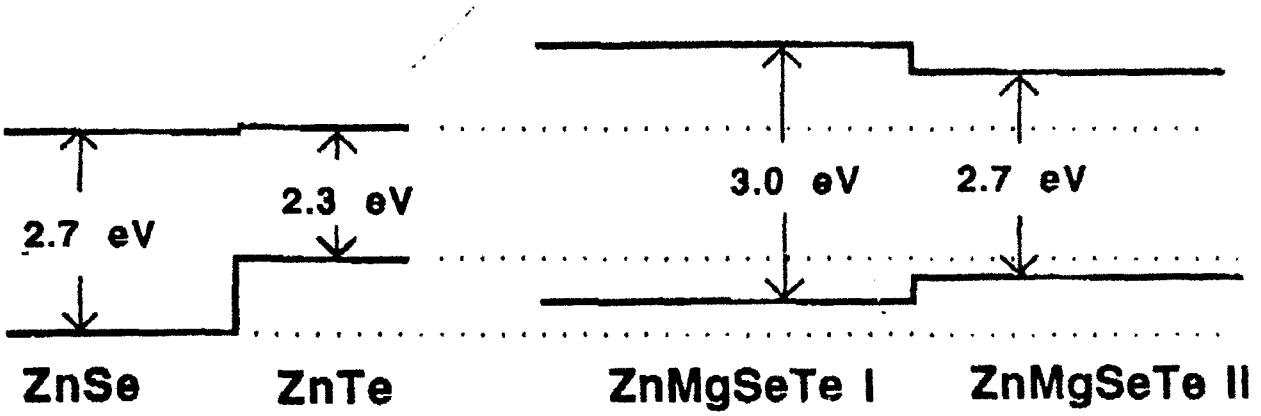


Fig. 4 Bandgap versus lattice constan of zincblende II-VI binaries and ternaries containing Mg. The dotted tieline connecting the ZnSeTe and MgSeTe valleys represents the region where amphoteric doping is expected. The vertical dashed lines indicate the location of the GaAs and InAs lattice constants.

• ZnMgSeTe Diode Laser Structure



ZnMgSeTe I : $Zn_{0.3}Mg_{0.7}Se_{0.4}Te_{0.6}$

ZnMgSeTe II : $Zn_{0.7}Mg_{0.3}Se_{0.2}Te_{0.8}$

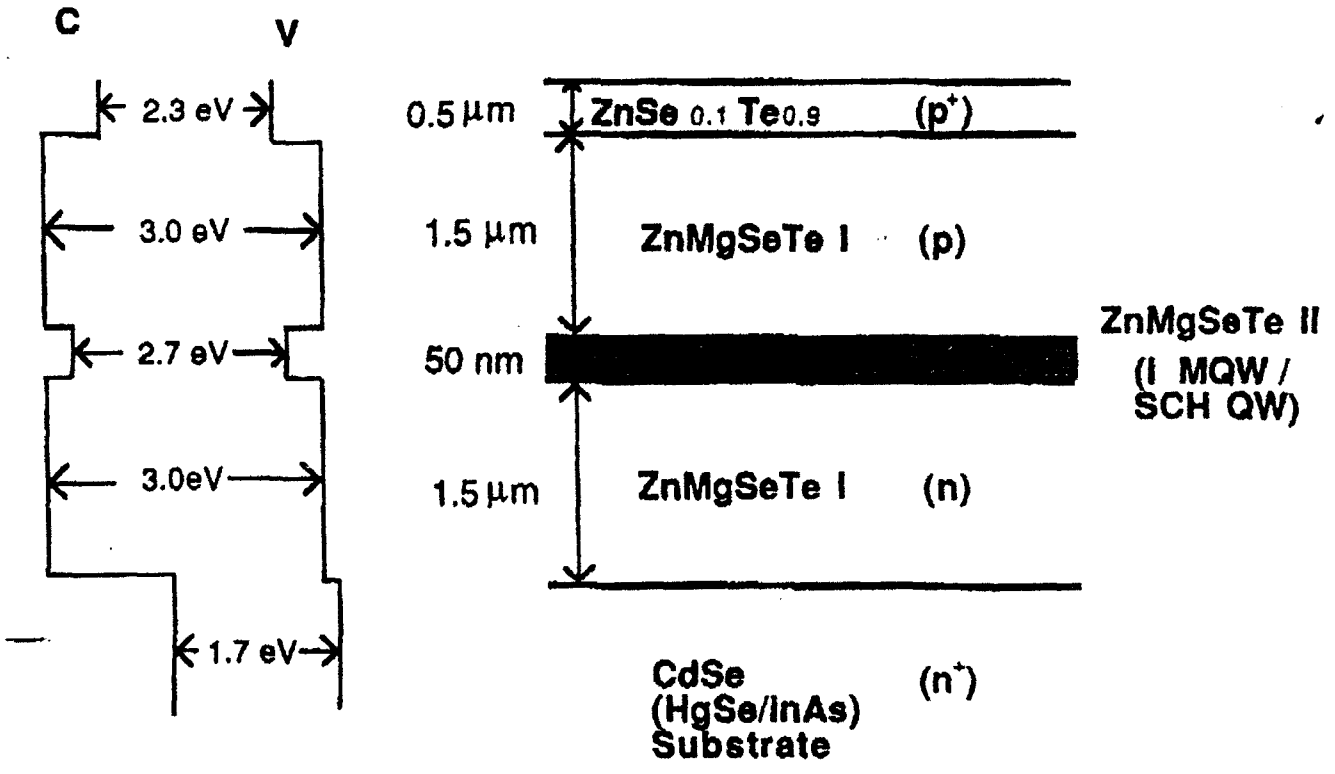


Fig. 5 ZnMgSeTe DH laser structure lattice matched to InAs for emission at 460 nm.

ZnSe based SCH QW Laser with ZnCaS Cladding
(Lattice matched with GaAs except QW)

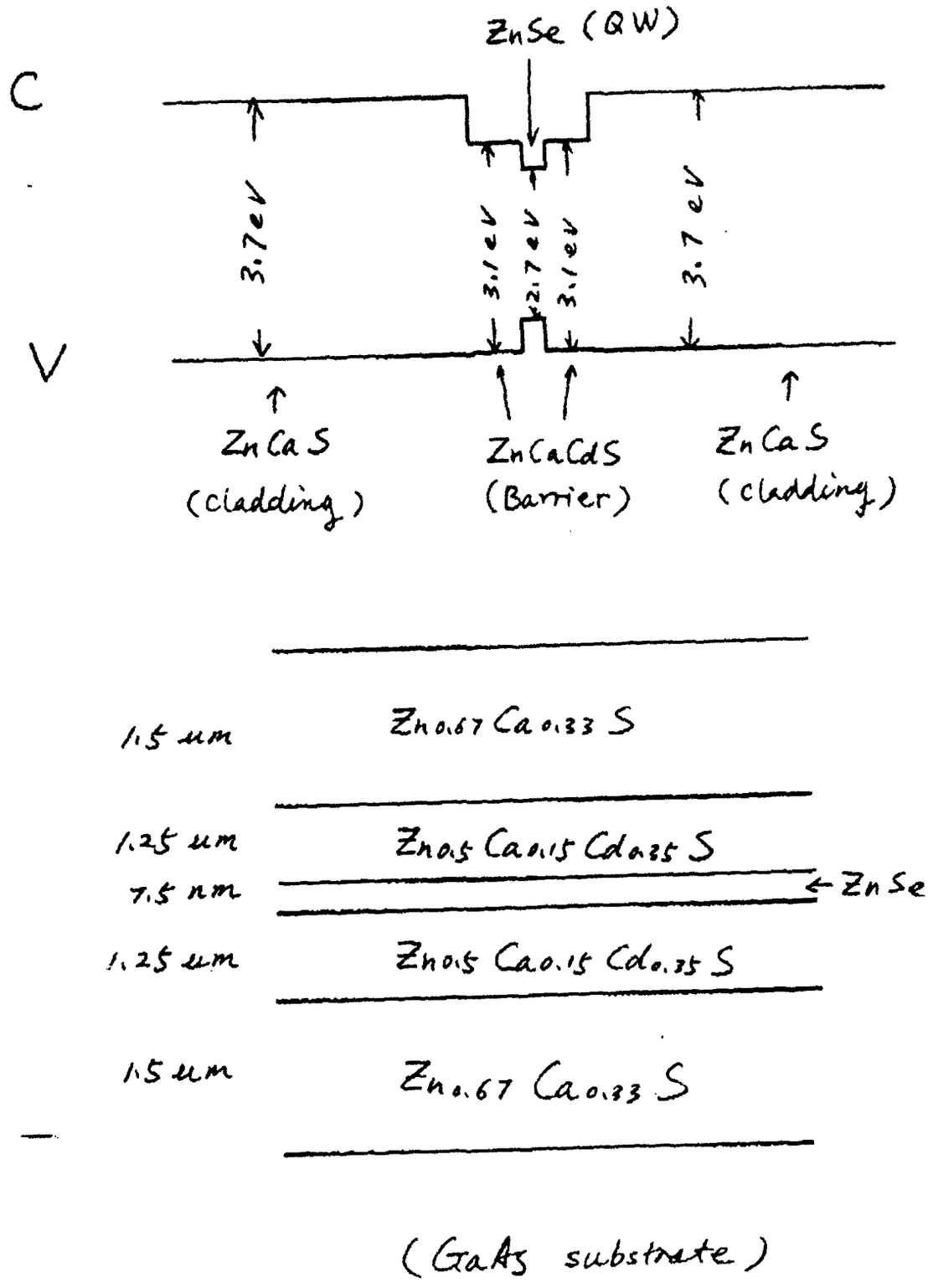


Fig. 6 ZnSe based SCH QW laser structure with ZnCaS cladding lattice matched to GaAs.

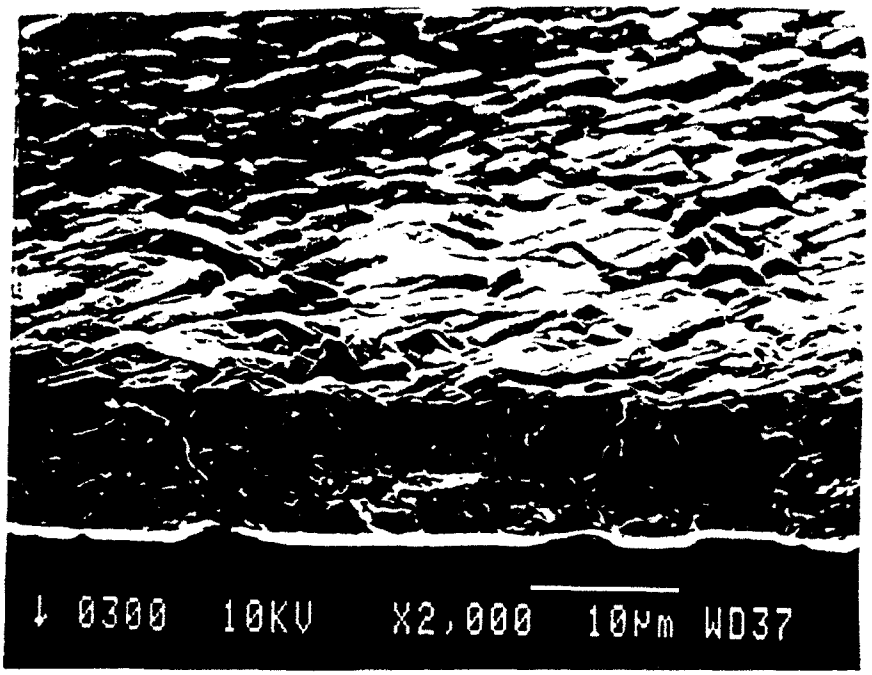


Figure 7. Scanning electron micrograph of a cleaved sample of conducting GaN on sapphire. The GaN is about 9 µm thick.

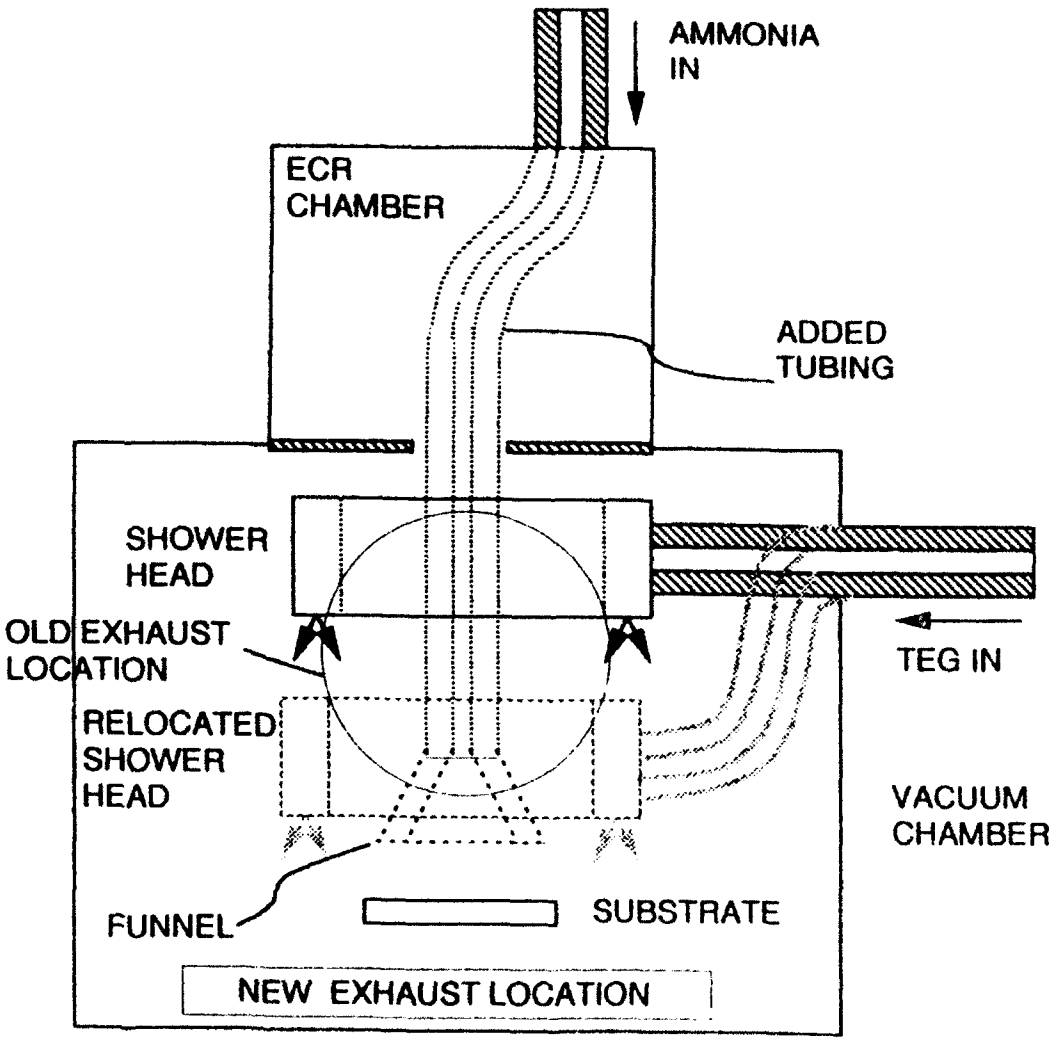


Fig. 8 Proximity gas delivery modifications.